Cement & Concrete Composites 30 (2008) 1013–1019

Contents lists available at ScienceDirect

Cement & Concrete Composites

journal homepage: www.elsevier.com/locate/cemconcomp

The effect of bentonite/cement mortar for the stabilization/solidification of sewage sludge containing heavy metals

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ARTICLE INFO

Article history:
Received 14 January 2007
Received in revised form 3 March 2008
Accepted 20 March 2008
Available online 29 March 2008

Keywords:
Cement
Bentonite
Stabilization/solidification
Leaching tests
Heavy metals

ABSTRACT

This study examines stabilization/solidification (S/S) techniques using a bentonite/cement mortar. These techniques are usually applied for the stabilization of sewage sludge, containing heavy metals such as Cu, Zn, Pb. Due to the high organic content of sludge, bentonite had been added in order to stabilize the system.

For this purpose, $4 \times 4 \times 16$ cm mortar prism samples were prepared. Their composition was: 50% w/w sewage sludge (primary sewage sludge from Psyttalia Athens and secondary biological sewage sludge from Metamorphosis Athens), 30% w/w cement CEMI 42.5 and finally 20% w/w bentonite. The samples were cured for 28 days at 25 °C and compressive strength was tested. Highest strength and lowest leachability were the criteria for selection of the optimum product by the S/S technique.

An extensive study using several characterization techniques focusing on hydration reactions was carried out. The instrumental analysis included: X-ray diffraction analysis, thermal analysis (TGA, DTA), electron scanning microscopy (SEM), infrared analysis (FT-IR) as well as tests for the toxicity characteristic leaching procedure (TCLP). The S/S products had been proven throughout the study as a viable solution for stabilizing heavy metals. They can be used in many applications such as in landfill liners, slurry walls and building blocks.

1. Introduction

Pollution caused by heavy metals is one of the most serious environmental problems, endangering fauna equilibrium. Heavy metals are stable and persistent environmental contaminants, as they cannot be degraded or physically neutralized.

Sludge contamination by heavy metals emerged as one of the most serious drawbacks encountered in the use of sewage sludge as a natural fertilizer [1]. Several researchers have studied the possibility of using natural clays for heavy metal ions immobilizing, due to their low cost and their large availability. Bentonite is one among these clays and it can be found as ingredient in the most cement blends around the world [2].

Bentonites are argillaceous materials that can be effectively employed as adsorbents for many wastewater pollutants, namely heavy metal ions and organic compounds due to the fact that they exhibit an enormous surface area when they are hydrated. This outstanding capability is due to the presence of the mineral montmorillonite and its structure, which is a determinant factor for the clay's properties. Bentonite presents strong colloidal properties and its volume increases several times when coming into contact with water, forming a gelatinus and viscous liquid. The special properties of bentonite (hydration, swelling, water absorption, viscosity, thixotropy) render it as a valuable material for a wide range of uses and applications [3].

Depending on the nature of their original formation, bentonites contain – in addition to montmorillonite - a variety of accompanied minerals that may include kaolinite, quartz, feldspar, calcite and gypsum. Their presence affects the industrial bentonite value, reducing or increasing its price according to the relevant application.

Depending on the amount and type of clay minerals present in the bentonite, the availability of alumina differentiates as follows: in kaolinite clays, the large amount of available alumina is released into the high pH solution at a high rate forming large amounts of ettringite which lead to large expansions (19% in the vertical direction). In contrast, montmorillonite clay's smaller alumina content, is released into the high pH solution at a five times slower rate, forming ettringite with no swelling development [4].

Stabilization/Solidification (S/S) is known as one of the most popular techniques for the treatment of hazardous waste and it

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doi:10.1016/j.cemconcomp.2008.03.001

has been used for decades an encapsulation material, prior to the disposal of radioactive and hazardous wastes [5,6].

Cement-based S/S is effective for inorganic wastes, but this is not appropriate for the treatment of waste with high organic content. This is because the interactions occur between the organics contaminants and the cementitious matrix, affecting the process (e.g. setting time) and the properties of the stabilized product. Many organic compounds are widely known to have a retarding effect on the cement hydration reaction and adversely affect on the microstructure, influencing the mechanical and the leaching properties of the cementitious materials [7]. One of the possible solutions to this problem engages the use of bentonite in conjunction with conventional cement-based techniques.

Clay is added in order to adsorb the organic materials and chemically bind them into the waste. In that way, when the cement is added, the organic materials do not interfere anymore, following the usual hydration reactions. Thus, the organic materials are held within the organophilic clay, while the clay itself is physically entrapped within the cementitious matrix [8].

The aim of the present study is to illustrate that the cement based S/S process techniques using bentonite can be effectively applied in order to sufficiently treat sewage sludge containing heavy metals and also to assess the properties of the S/S products in order to apply them in landfill liners, building blocks and slurry walls.

2. Experimental program

2.1. Materials and methods

2.1.1. Bentonite characterization

The bentonite used in this work originates from a S&B Industrial Minerals S.A. bentonite deposit quarry in Milos island, in Greece. The chemical composition is shown in Table 1. The presence of the clay mineral montmorillonite as well as quartz and calcite impurities as detected by XRD analysis is shown in Fig. 1.

2.1.2. Types of sludge

Two types of sludge were used for the experiments. The first type of sludge was a primary sludge from Psyttalia wastewater treatment plant, which serves the major Athens area and which also receives a considerable amount of industrial wastes. The second type of sludge was a mixture of a primary and a secondary (biological) sludge, originated from the Metamorphosis wastewater treatment plant where industrial wastes were also treated.

Table 1
Chemical composition of bentonite, wt%

LOI[*]	SiO_2	A_2O_3	TiO_2	Fe_2O_3	MgO	CaO	Na_2O	H_2O	Total
8.75	53.72	19.12	0.85	4.93	3.29	5.28	3.64	0.44	100.0

[*] LOSS on ignition at 1100 °C.

Both types of sludge were characterized using the standard methods of analysis [9]. Total organic carbon (TOC) was measured by a titrimetric method [10] and the concentration in heavy metals was obtained using atomic absorption spectrometry (AAS Perkin Elmer 3300). The analysis' results are shown in Table 2. Leaching of heavy metals was measured by the toxicity characteristic leaching procedure (TCLP) test [11].

2.1.3. Other materials

For the preparation of the referred specimens, Portland cement (CEMI 42.5 type) was used as binder, while standard sand (according to EN169-1) was used as an aggregate.

2.1.4. Sample preparation

All the samples were prepared by mixing the binder and the other components, then adding the proper amount of water, in order to obtain equal workability of all the mixtures. The mixing procedure was the same for all mortars and it is described as follows: first, the sludge sample (in dry or wet conditions) was mixed with water (which was calculated according to previous work [12]). Then, the binder mixture was added and finally, the sand [13].

The sludge/binder ratios examined were:

(a) 1:1 for dry sludge from Psyttalia or Metamorphosis;
(b) 0.34:1 for wet sludge from Psyttalia;
(c) 0.30:1 from Metamorphosis sludge.

Based on these ratios, $4 \times 4 \times 16$ cm mortar prism samples were prepared. The composition of the mortars samples is given in Table 3.

Paste of similar composition, but without addition of sand, was prepared in order to be used for XRD analysis, Thermal analysis (TGA, DTA), FT-IR analysis and finally for SEM analysis.

X-Ray diffraction analysis experiments were carried out using a Siemens D5000, and their evaluation were made using Siemens DIFFRAC A.T. Search Program software.

Thermal analysis experiments were carried out using a Mettler Toledo TGA/SDTA851[e] measuring module, with temperature

Table 2
Characteristics of sludges

Sludge property	Psyttalia sludge	Metamorphosis sludge
Moisture content (%)	66.5	69.7
TOC (%)	30.0	10.0
pH	7.4	7.0
Heavy metals (mg/g)[a]		
Cr	0.57	0.47
Cu	0.26	0.46
Fe	8.12	13.6
Ni	0.108	0.23
Pb	0.14	1.09
Zn	1.95	2.4

[a] Concentration of heavy metals (mg/g dry sludge).

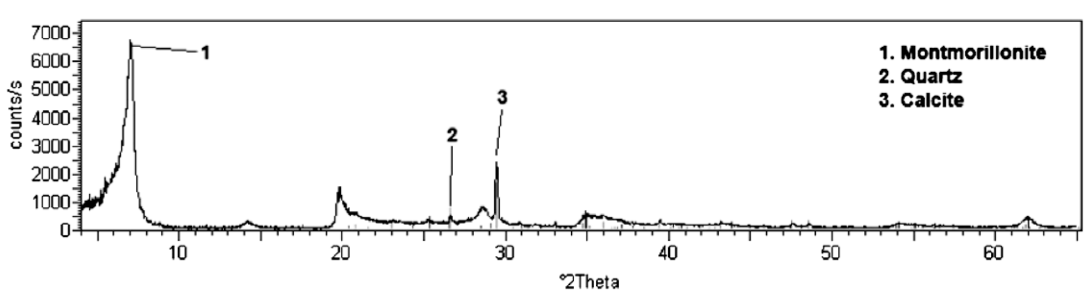

Fig. 1. XRD sample of bentonite.

Table 3
Composition of the mortars

Mortar	Sludge/ binder	Sludge solids/ binder	Sludge solids/ cement	Dry sludge (g)	Cement (g)	Bentonite (g)	Sand (g)	Water (ml)
Dry Psyttalia/cement	1/1	1/1	1	225	225	0	1350	345
Dry Psyttalia/cement/bentonite	1/1	1/1	1.7/1	225	135	90	1350	425
Dry Metamorphosis/cement	1/1	1/1	1/1	225	225	0	1350	325
Dry Metamorphosis/cement/ bentonite	1/1	1/1	1.7/1	225	135	90	1350	425
Wet Psyttalia/cement	1/1	0.34/1	0.34/1	75.4	225	0	1350	180
Wet Psyttalia/cement/bentonite	1/1	0.34/1	0.56/1	75.4	135	90	1350	200
Wet Metamorphosis/cement	1/1	0.30/1	0.30/1	68.2	225	0	1350	180
Wet Metamorphosis/cement/ bentonite	1/1	0.30/1	0.51/1	68.2	135	90	1350	200

accuracy ±0.5 °C and temperature reproducibility of ±0.3 °C. The samples were placed in an alumina (Al_2O_3) pan (with no lid) of 70 μl volume capacity and heated under a dynamic linear heating rate of 10 °C/min, under a flow rate of 50 ml/min nitrogen (N_2), from 25 °C up to 700 °C.

Microstructural investigation was conducted using a scanning electron microscope (Microscope JEOL JSM-5600 with Oxford Link Isis300). All the samples weight approximately 30 mg (±1 mg).

For material characterization and for distinguishing the different types of interactions which occurred, FT-IR analysis was used. The experiments were carried out in an EXCALIBUR Series FTS 3000MX of BioRad.

3. Results and discussion

3.1. Compressive strength results

The prepared samples were cured for 28 days at 25 °C and their compressive strength was determined, according to the methods of the European Standard EN196-1 [14]. The results are shown in Table 4, from where it can be noticed that four (4) out of the eight (8) mixtures, displayed compressive strengths which exceeded the minimum limit of 350 kPa at 28 days [11]. These are the mixtures containing cement/sludge and cement/sludge/bentonite with wet sludge from Metamorphosis and Psyttalia.

Bentonite's effect on both sludges was significant as the samples showed higher compressive strength than 350 kPa but lower than the cement sample due to the substitution of cement by bentonite.

Increased values of compressive strength were observed when Metamorphosis sludge was used. This can be attributed to the lower organic carbon content of Metamorphosis sludge (considering that it was a secondary sludge compared to Psyttalia's primary sludge).

3.2. XRD analysis results

The XRD analysis for all specimens that met the minimum compressive strength limit of 350 kPa, was very similar. All mixtures displayed characteristic peaks of C–S–H, $Ca(OH)_2$, ettringite, C_3S, C_2S.

The results of mixtures composed of Psyttalia sludge and cement are given in Fig. 2 and they can be summarized as follows: the main hydration products of cement were C–S–H, $Ca(OH)_2$ and ettringite (which were formed instead of monosulfate). $Ca(OH)_2$ is produced simultaneously with C–S–H when the reactions of C_2S and C_3S with water take place. The formation of C–S–H occurs, which along with ettringite, leads to the hardening of the cement [13,15].

Table 4
Compressive strength tests results of mortars

Samples	Compressive strength, kPa (28 days)
Dry Psyttalia/cement	89.05
Dry Psyttalia/cement/bentonite	85.84
Dry Metamorphosis/cement	119.47
Dry Metamorphosis/cement/bentonite	98.91
Wet Psyttalia/cement	920.0
Wet Psyttalia/cement/bentonite	440.41
Wet Metamorphosis/cement	1426.0
Wet Metamorphosis/cement/bentonite	450.53

3.3. Thermal analysis

Thermogravimetry (TGA) and differential thermal analysis (DTA) were done. As shown in Fig. 3 the curves can be interpreted by focusing into the following, which are representing different kinds of reactions:

1. up to 100 °C: removal of water from hydrated products;
2. up to 300 °C: different stages of C-S-H dehydration;
3. the endothermic-peak at 450 °C is due to the dehydroxylation of calcium hydroxide which reveals, the presence of $Ca(OH)_2$ according to the following reaction:

$$Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^-$$

4. the endothermic-peak at 750 °C is due to the decarbonation of calcium carbonate:

$$CaCO_3 \rightarrow CaO + CO_2$$

5. the endothermic-peak at 950 °C, without change of weight, is attributed to SiO_2 conversion, from anhydrous crystalline to β-SiO_2 and cristobalite.

The main conclusion that can be drawn from all the above is that the hydration of the cement is well underway and progressing.

3.4. Scanning electron microscopy (SEM)

Scanning electron micrograph results of the cement/sludge mixtures aged 28 days is shown in Fig. 4. Typical hydration products can be identified, such as ettringite (needle-like crystals), calcium silicated hydrate (gel-like flocks) and finally calcium hydroxide (fibrous-like crystals). In the centre of the Fig. 4, a large grain of almost non reacted sludge with hydration products growing on its surface is also seen.

Fig. 5 is related to the bentonite/cement sludge mixtures. The morphology of this system is very similar to the one mentioned above and the same phases can be seen. Furthermore, large lath-like crystals 10–100 mm long and several micrometers (mm) thick, has been formed in a relatively low pH environment, as it has been

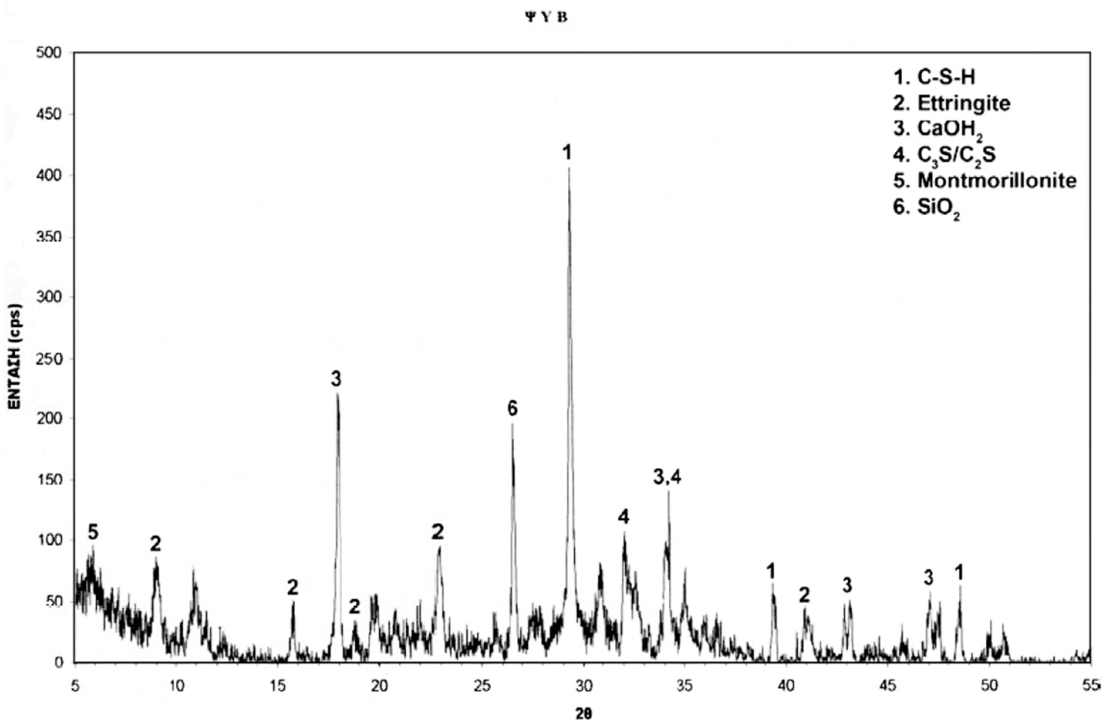

Fig. 2. XRD sample of Psyttalia sludge/cement/bentonite.

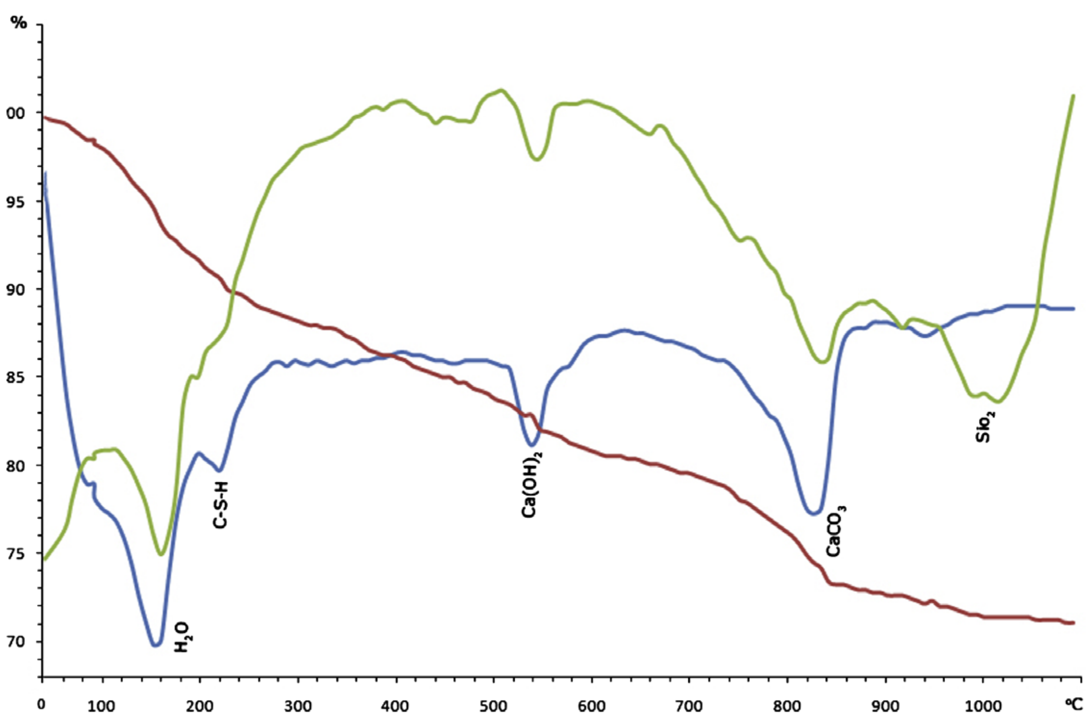

Fig. 3. TG, DTG, SDTA sample of Psyttalia sludge/cement/bentonite.

observed by SEM techniques. The increase of the proportion of large ettringite crystals increased the compressive strength (Table 4) and also no volume change was noticed, one that could have caused macroscopic cracking [4].

However, in comparison to the cement/sludge mixtures, the microstructure was obviously more open, due to the lower cement content. Further comparison to the cement/bentonite/sludge mixtures leads us to the conclusion that the porosity of bentonite increased.

3.5. Infrared analysis

The FT-IR spectrum of bentonite is showed in Fig. 6 trace A. The spectrum of bentonite shows typical infrared bands of

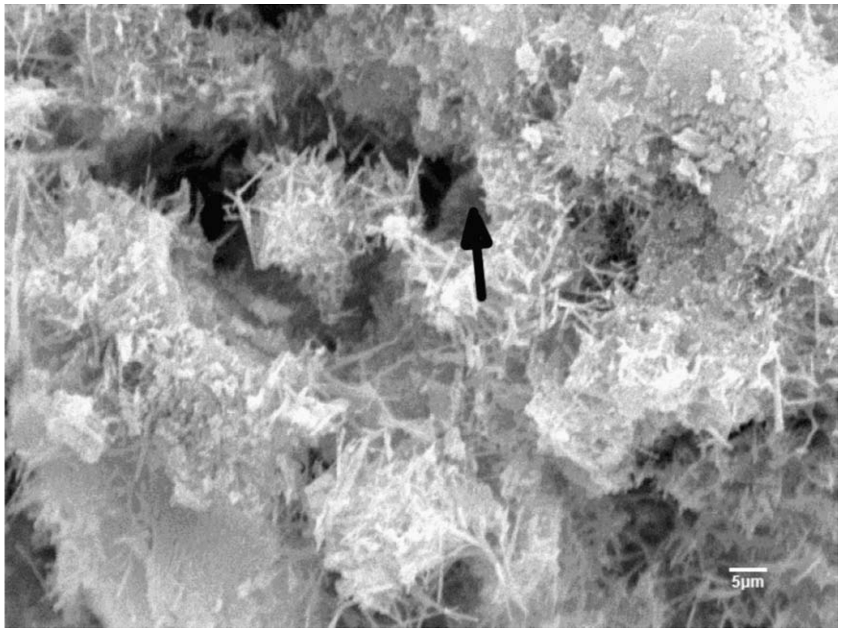

Fig. 4. SEM sample of Psyttalia sludge/cement (1000×).

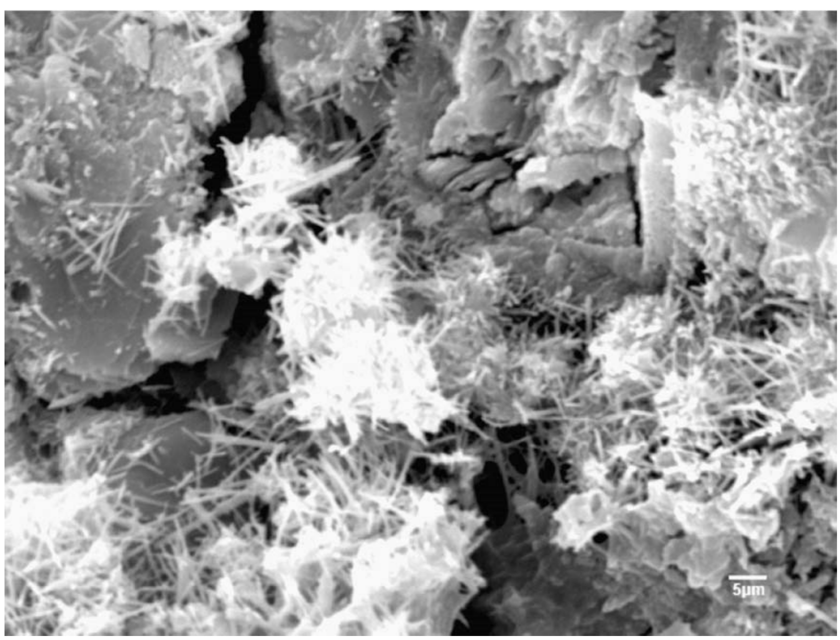

Fig. 5. SEM sample of Psyttalia sludge/cement/bentonite (1000×).

montmorillonite, due to OH^- stretching at 3432 cm^{-1} and Si–O–Si bending at 1041 cm^{-1}. Bentonite/mixtures also showed a wide and intense band at 1441 cm^{-1} and a weaker band at 876 cm^{-1} which is attributed to $CaCO_3$. The presence of organic load was detected between 2859 and 2961 cm^{-1} [3].

Fig. 6 trace B of the FT-IR spectrum of the bentonite/cement/sludge mixtures exhibited less absorption at 3429 cm^{-1} and higher absorption at 1426 cm^{-1} and 873 cm^{-1} due to $CaCO_3$ presence. Also, the FT-IR results showed that no new bands were formed between bentonite/cement/sludge mixtures after S/S techniques. The lack of new picks in the FT-IR spectra leads to the conclusion that physical absorption took place.

3.6. Leaching tests results

The leaching behavior of heavy metals in these cement-based waste materials was studied by toxicity characteristic leaching procedure (TCLP) described by USEPA [11].

The TCLP tests were carried out for the samples with wet sewage sludge, since they met the minimum value of compressive strength. Following this, the composition of samples was: 50% sewage sludge, 20% bentonite and 30% cement. The results of leaching tests are presented in Table 5.

The TCLP tests, as shown in Table 5, indicate the following: high retention percentages of heavy metals for both sewage sludges of

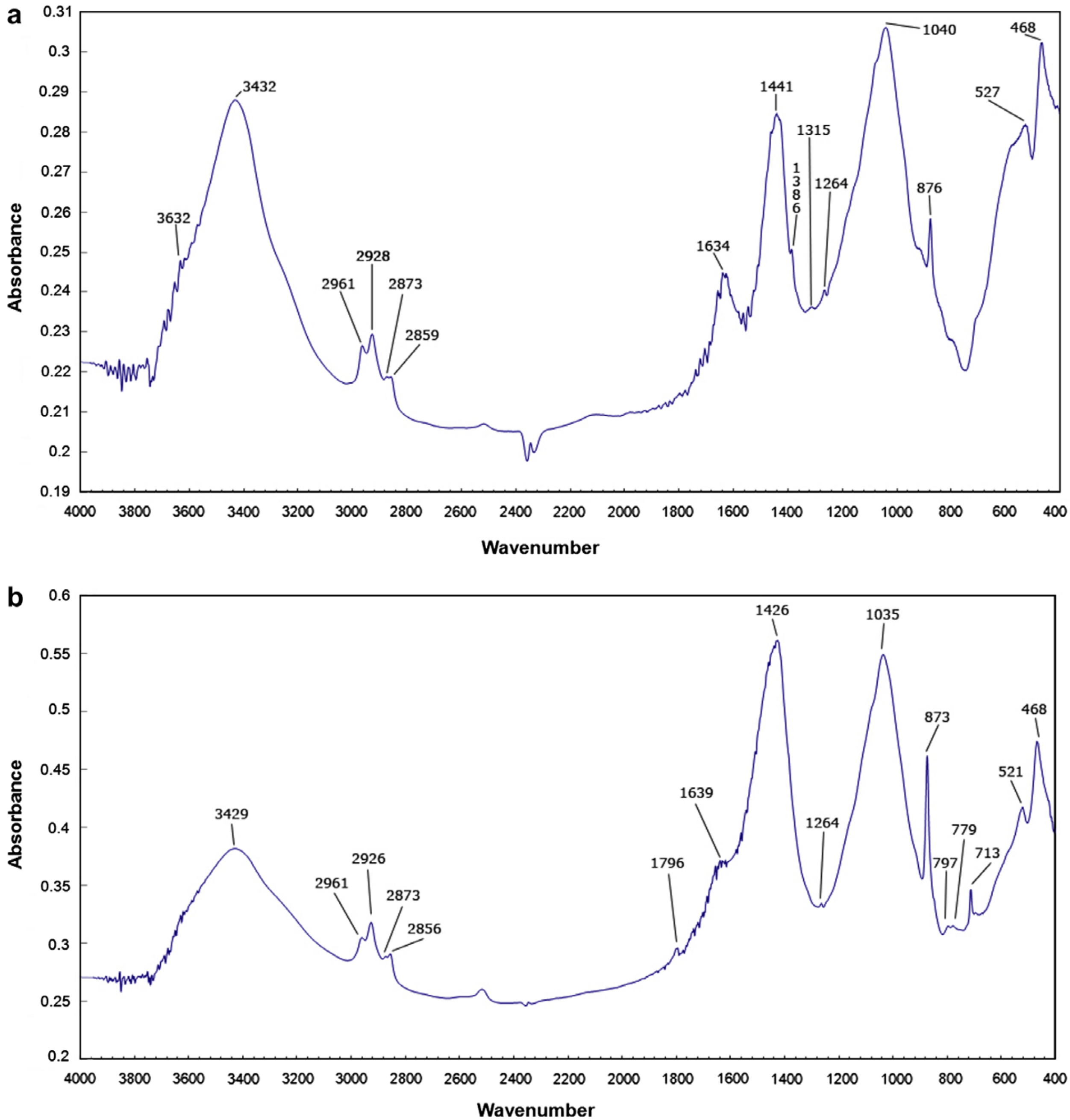

Fig. 6. Trace A: FT-IR sample of bentonite. Trace B: FT-IR sample of Psyttalia sludge/cement/bentonite.

Table 5
TCLP test results and heavy metals retention percentage for Metamorphosis and Psyttalia sludge

	Sludge solids (%)	Cu		Fe		Zn		Ni		Cr		Pb		pH
		ppm	%	ppm	%	ppm	%	ppm	%	ppm	%	ppm	%	
Psyttalia	100	1.05	0	8.3	0	3.6	0	1.13	0	1.2	0	0.4	0	7.40
Wet Psyttalia cement	16.75	0.30	71	0.2	98	1.01	72	1.02	10	0.05	96	0.05	88	7.00
Wet Psyttalia cement/bentonite	16.75	0.26	76	0.16	98	0.9	75	0.51	55	0.03	97	0.04	90	7.00
Metamorphosis	100	2.43	0	9.40	0	4.2	0	2.22	0	0.73	0	0.3	0	6.91
Wet Metamorphosis cement	15.15	0.21	92	0.51	95	1.25	70	0.69	69	0.57	22	0.04	87	7.00
Wet Metamorphosis cement/bentonite	15.15	0.10	96	0.29	97	1.18	72	0.53	76	0.27	63	0.03	90	7.00
Limits [16]		0.6				1.2		0.12		0.1		0.15		

bentonite/cement/sludge mixtures and in specific, concentrations of Cu, Fe, Zn and Pb were found to be below the detection limits according to European Council decisions [16].

Furthermore, the use of bentonite improved the retention of above mentioned heavy metals. This fact can be attributed to the bentonite's strong detention capacity, which could neutralize the extraction solution and limit the metal leaching process.

4. Conclusions

Mortars with 50% wet sludge (from Psyttalia or from Metamorphosis), 30% cement and 20% bentonite produced by S/S techniques showed higher compressive strength than the minimum limit of the 350 kPa at 28 days.

XRD analysis clearly showed that hydration products were well formed.

Thermal analysis verified the above result.

SEM clearly identified typical hydration products, such as ettringite (needle-like crystals), calcium silicate hydrate (gel-like flocks) and calcium hydroxide (fibrous-like crystals).

FT-IR analysis in all cases showed that only physical adsorption took place and that no chemical bonds were formed during S/S techniques.

The TCLP tests have showed high retention percentage of heavy metals in the bentonite/cement mixture and leachate lower heavy metals concentrations than the minimum allowed value. The addition of bentonite reduced the leachability and toxicity of the containing metal in sewage sludge.

Conclusively, it can be suggested that the treatment of 50% wet sewage sludge with 20% bentonite and 30% cement was sufficient to stabilize/solidify and to produce a material that can be applied as additive in landfill liners, slurry walls and building blocks.

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